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SYNTHESIS AND CHARACTERIZATION OF COPOLYMERS OF NYLON 11 AND NYLON 12

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ABSTRACT

A series of copolymers was prepared from 11-aminoundecanoic and 12-aminododecanoic acids by melt-condensation at 210 °C in sealed tubes under vacuum. Mole percentages of nylon 12 monomer were 0, 15, 35, 50, 65, 85, and 100 % in the feed. The amide group was labelled using ^{15}N-labelled amino acids available through the Gabriel synthesis (only the 1:1 copolymer was enriched with nitrogen-15). Solid-state ^{13}C (at 100.6 MHz) and ^{15}N (at 20.3 MHz) NMR spectroscopy, differential scanning calorimetry, wide-angle x-ray diffraction, and infrared spectroscopy were used to characterize the copolymers. Solid-state ^{15}N NMR spectra showed a smooth shift of the main peak position from 84 ppm for α-nylon 11 to 89 ppm for γ-nylon 12 for the as-prepared copolymers. Similar behavior was seen for amide V and VI modes which are sensitive the α- and γ-crystal forms. Carbon-13 NMR T_1 measurements showed that the most mobile sample was the 65:35 nylon 11-co-12 polymer. An annealed, solution-cast film of the 50:50 copolymer afforded material with a T_{1N} value of 349 s, similar to annealed nylon 11 and nylon 12 homopolymers. Melting point and heat of fusion depressions were observed for the copolymer series with the 65 mol-% nylon 12 copolymer having the lowest % crystallinity and T_m at 148 °C. Solid-state NMR

measurements indicated that the α-crystal form dominates as the stable polymorph up to 65 mol-% nylon 12 in as-polymerized samples, then the γ-phase predominates. The WAXS pattern for the 65 mol-% nylon 12 sample shows a sharp peak at 2θ = 21.3, overlapping a broad peak centered at 2θ = 21.0. This is consistent with the spacing seen for γ-nylon 12. The 1:1 copolymer was shown to be polymorphic, like the homopolymers, with an γ-like phase formed upon solvent casting, and an α-like phase dominating for as-polymerized material and precipitated flakes.

Introduction

Copolymers in general provide opportunities for developing new materials with tailored properties. The synthesis of copolymers requires the determination of reactivity ratios,[1,2] which in turn allow controlled modification of polymer properties such as solubility of rigid-rod polymers,[3,4,5] the effect of ionizable groups on ion binding,[6] the isomorphic behavior of biodegradable copolyesters,[7,8,9,10] the placement of otherwise intractable functionalities in a tractable backbone,[11] and the modification of commercially available polymers to enhance their blend behavior.[12]

Our interest in random copolymers stems from investigations of semi-crystalline polyamides[13,14,15] using solid-state NMR to determine types of crystal phases present. Many random copolyamides are isomorphic and are able to crystallize despite a mismatch of repeat unit lengths. The crystallinity developed is different than the traditional type. For example, differential scanning calorimetry generally underestimates the amount of crystallinity due to the lack of characterization of the isomorphic crystalline phase that has a heat of fusion different from the parent homopolymers. WAXS and density

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measurements give improved measures of overall crystallinity, although they are also limited in sensitivity in terms of evaluating crystallite size and perfection since each method sees the polymer on a different level of organization.

Nylon 11 crystallizes into the α-phase from the melt while nylon 12 adopts the γ-phase. In the α-phase, the polymer chains are arranged in an anti-parallel manner with the amide units coplanar with the zig-zag methylene segments, while the γ-phase chains are packed parallel to each other with the amide units twisted from the plane of the aliphatic segments by ca 60°. Our experience with solid-state NMR in characterizing nylon homopolymers suggested that such a molecular level probe of polymer chain packing behavior might provide insight into isomorphic crystallinity in nylon copolymers such as those obtainable from polycondensation of the amino acid monomers for nylons 11 and 12.

EXPERIMENTAL

Solvents were reagent grade and used as received. The amino acids were purchased from Aldrich Chemical Company and recrystallized from boiling, deionized water three times before use. The ^{15}N-labelled amino acids were prepared in several steps using labelled potassium phthalimide, 11-bromoundecanoic acid,[14] and 12-bromododecanoic acid.[15]

Mixtures of the amino acids were sealed under vacuum in glass tubes and polymerized at 210 °C for 4 h using a Wood's metal bath as a constant temperature medium. The following mole percentages of amino acids (C_{11}:C_{12}) were used with the sample designation given in parentheses: 100:0 (PA-1), 85:15 (PA-2), 65:35 (PA-3),

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50:50 (PA-4), 35:65 (PA-5), 15:85 (PA-6), and 0:100 (PA-7). The colorless polymer plugs were carefully removed from the glass tubes after cooling. Thin films of the as-polymerized polymers removed from the glass tubing were used for FTIR measurements.

A sample of PA-4 was dissolved in a mixture of 2,2,2-trifluoroethanol (TFE) and methylene chloride (3:2 by volume), cast onto glass and the solvent allowed to evaporate (PA-4CF). Another portion of the PA-4 solution was precipitated into rapidly stirring diethyl ether, collected, and dried (PA-4PF). PA-4CF and PA-4PF were annealed under vacuum at 115 °C for 2 days, and designated PA-4CA and PA-4PA, respectively.

Differential scanning calorimetry measurements were made using a Perkin-Elmer DSC-7 equipped with a microcomputer. The instrument was calibrated immediately prior to use with tin and indium standards. Data were collected at 10 °C/min in aluminum pans. FTIR spectra (as-polymerized thin films) were obtained using a Bruker IFS-88 at a resolution of 0.5 cm^{-1} (64 scans per sample). Wide-angle X-ray diffraction data were obtained using a Siemens XPD-700P polymer diffraction system equipped with a two-dimensional, position sensitive, area detector, and background corrected using the GADDS™ software package.

Solid-state NMR spectra were obtained using a Bruker MSL-200 for ^{15}N operating at 20.287 MHz and a Bruker MSL-400 for ^{13}C operating at 100.614 MHz. The parameters used to collect the spectra are shown in Table 1. Samples were placed in fused zirconia rotors and spun with dry air. Spin-lattice relaxation data were collected using the method developed by Torchia.[16]

Table 1. NMR Spectrometer Acquisition Parameters

Parameter	^{13}C	^{15}N
^{1}H 90°-pulse	5.5 µs	5.7 µs
X 90°-pulse	5.3 µs	5.6 µs
contact pulse	1.0 ms	1.0 ms
ringdown delay	14 µs	30 µs
acquisition time	45 ms	68 ms
recycle delay	3 s	5 s
spinning rate	5 kHz	3 kHz
# of scans	400 - 800	20 - 40 k
data size	8 kbytes	8 kbytes
time domain size	4 kbytes	2 kbytes
sweep width	300 ppm	600 ppm
stator diameter	4 mm	7 mm

Results and Discussion

A single report[17] on the synthesis of nylon 11-co-12 appears in the literature in which a 1:1 copolymer was prepared by reaction of 11-aminoundecanoic acid with laurolactam under melt conditions at 250 °C. Solution ^{13}C NMR results suggested that no resolution of the carbonyl carbons could be obtained due to the similarity in length of the carbon monomer framework. No other characterization data for this copolymer was given. Our attempts at repeating this procedure mostly gave nylon 11 highly plasticized with the 12-carbon lactam. No copolymer was ever achieved under conditions similar to those listed in the reference.

Other reports[18,19] of A-B type nylon copolymers describe syntheses, characterization, and physical properties. Almost all of the copolyamides were reported to be essentially random. Melting point depressions and decreases in crystallinity were observed and increases in % elongation were seen with a concomitant decrease in modulus. However, many of the reports did not cover the full range of copolymer compositions.

The copolymers obtained from polymerization of the 11- and 12-carbon amino acids were expected to be random since the starting monomers possess similar structures and end-group reactivities. The monomer melting prints are a few degrees apart and homopolymers are readily obtained from each under conditions similar to those used for copolymer synthesis. The polymer plugs obtained were very tough and required careful cutting with a razor blade. While the two homopolymers were not readily soluble in the TFE-CH$_2$Cl$_2$ mixture, all of the copolymers were. The solution ^{13}C NMR spectrum (not shown here) of the 1:1 copolymer showed a single carbonyl peak at 176.9 ppm. This is in agreement with the single peak observed by Kricheldorf for his polymer, although he used fluorosulfonic acid as solvent.[17] However, our solution NMR experiments on the sample obtained from 11-aminoundecanoic acid and laurolactam showed peaks for both lactam and homopolymer nylon 11. The DSC results showed a melting endotherm for lactam and a slightly depressed T$_m$ for nylon 11, but no obvious T$_m$ for copolymer. Based on these results, we chose to use the commercially available amino acids for copolymer synthesis rather than attempting further reactions with the lactam.

Thermal Analysis

The thermal data for the copolymer series is shown in Table 2, while the T_m and % crystallinities (based on ΔH data) are plotted in Figure 1 for homopolymers and samples PA-1 through PA-7. It is clear that the melting points decrease with increasing comonomer content on moving away from the homopolymers with a minimum near 65 mol-% nylon 12 units. This is also where the estimated percent crystallinity reaches its minimum for the as-prepared samples. The percent crystallinity was calculated after the manner of Garner and Fasulo[20] using the ΔH_f of the pure homopolymers.

Table 2. Nylon 11-co-12 thermal data[a] for all as-obtained and several treated samples

SAMPLE	ΔH (J/g)	onset T_m (°C)	T_g (°C)	% cryst.
PA-1	54	183	45	24
PA-2	39	175	43	22
PA-3	38	160	37	17
PA-4	34	152	43	17
PA-5	31	148	42	14
PA-6	46	163	41	20
PA-7	65	171	41	30
PA-4CF	65	146	42	29
PA-4PF	50	148	42	22
PA-4CA	75	146	[b]	33
PA-4PA	55	151	[b]	24

[a] - data averaged over three samples for first runs; % crystallinity calculated according to the method used for nylon 6-co-12[20]
[b] - no glass transition temperature observed for these samples on the first run

We speculate that, as the amount of comonomer increases, the less perfect and/or the smaller the crystallites become, causing a depression in the melting points. No multiple melting peaks were observed by DSC, suggesting that separate domains of homopolymer segments did not form. However, the thermograms of the homopolymers and copolymers showed a melting endotherm superimposed on a crystallization exotherm, suggesting the melting of the less-perfect crystallites followed by simultaneous formation and melting of more perfect crystalline domains.[21] On the second and third DSC runs, no crystallization exotherms were observed as has been reported for nylons 6-co-8 and 6-co-12 at compositions up to 30 mol-% nylon 8 and nylon 12, respectively,[18c] and for 1:1 nylons 6-co-11, 6-co-12, 7-co-11, and 7-co-12.[22] Interestingly, the second and third run T_m's were only slightly reduced from the first run, although the ΔH and % crystallinity were reduced. It is clear that regardless of the <u>amount</u> of crystallinity inferred by the DSC data, the nature of the chain conformations and the type of crystalline packing that exists cannot be determined by thermal analysis.

Solid-State NMR

The solid-state ^{13}C CP/MAS and CPT1 NMR spectra of the copolymers (aliphatic regions only) are shown in Figure 2. The CP/MAS spectra contain peaks for both amorphous and crystalline domains, while the CPT1 spectra show only crystalline domain peaks. Examination of the spectra suggests that there is a smooth transition in peak positions going from PA-1, 100 mol-% nylon 11, to PA-7, 100 mol-% nylon 12. The chemical shift data from the CPT1 spectra are contained in Table 3. Nylon 11 crystallizes into the α-phase from the melt and nylon 12 into the γ-phase. Each has its own particular

chain conformations in extended chain crystallites,[23] and solid-state NMR is sensitive to these differences.

Table 3. Nylon 11-co-12 polymer chemical shift values from CPT1 spectra

SAMPLE	CO	C_N	C_α	C_{AT}	C_β	NH[a]
PA-1	173.7	42.5	35.8	33.4	27.5	85.2
PA-2	173.5	42.3	35.8	33.4	27.5	85.8
PA-3	173.6	41.5	35.8	33.3	27.4	86.3
PA-4	173.6	41.0	36.2	33.2	27.4	86.9
PA-5	173.4	40.2	35.9	33.4	31.0	86.9
PA-6	173.2	39.5	35.8	33.5	30.2	88.1
PA-7	173.3	39.6	35.9	33.5	30.2	88.9
PA-4CF	173.1	39.7	36.8	33.6	30.3	88.9
PA-4PF	173.5	40.1	35.9	33.3	28.0	87.0
PA-4CA	173.2	39.6	36.7	33.5	30.6	88.9
PA-4PA	173.5	40.8	36.4	33.3	27.7	86.9
PA-4PF[b]	173.9	40.5	36.9	30.9	[d]	87.1
PA-4 (sol)[c]	176.9	40.6	37.3	30.0	27.4	[e]

[a] - data taken from CP/MAS NMR experiments for both natural-abundance and isotopically enriched samples
[b] - data taken from HP/MAS experiments for both ^{13}C and ^{15}N
[c] - data collected for as-polymerized PA-4 in a mixture of TFE and CH_2Cl_2 at 75.465 MHz
[d] - peak not observed
[e] - data not collected

As we have described for nylon 7,[24] the carbon beta to the carbonyl (C_β) appears at 28 ppm in α-crystallites due to shielding effects of the oxygen atom in the carbonyl group. Others have seen similar behavior for nylon 6 polymorphs and have reported[25]

that the C_β peak in γ-crystallites appears near 30 ppm. Similarly, the carbon alpha to the nitrogen atom (C_N) appears near 43 ppm in α-crystals, while it is near 39 ppm in γ-crystals.

For the CPT1 spectra, the C_β peak at 27.5 ppm for PA-1 becomes less pronounced as the amount of comonomer is increased, appearing near 30.2 ppm for PA-5 through PA-7. Similarly, C_N moves from 42.5 ppm for PA-1 to 39.6 ppm for PA-7, consistent with a change from the α-phase to the γ-phase. This can be rationalized in terms of diminishing amounts of one type of crystalline phase in favor of the other. That is, as the amount of 12-aminododecanoic acid is increased in the monomer feed, the more the crystallites look like nylon 12 γ-phase crystallites. This can be seen more readily by examining the CPT1 chemical shifts of C_N which are plotted in Figure 3 against mol-% 12-aminododecanoic acid. The plot is nearly linear between the α-phase peak at 42.5 ppm and γ-phase peak at 39.5 ppm. Interestingly, the chemical shift of the C_{AT} peak at about 33.4 ppm remains fairly constant over the composition range, even though the two homopolymers contain different numbers of molecules per unit cell and crystallize into different unit cells.[23]

The solid-state ^{15}N CP/MAS NMR spectra are contained in Figure 4 and the chemical shift values are plotted in Figure 3. The spectra consist of overlapping peaks for the amorphous and crystalline domains. The α-phase peak appears at 84 ppm and that of the γ-phase at 89 ppm, with the broad amorphous peak centered near 86 to 87 ppm. It is clear the spectrum of PA-7 (pure nylon 12) consists of a sharp peak near 89 ppm overlapping a broad resonance at 86. The low level of crystallinity developed in PA-

1 (approximately 24 % by DSC), however, does not allow as-ready observation of crystalline and amorphous peaks. We know from previous work[13,14,15] with isotopically enriched polymer samples (which allow phase-selective observation of the amorphous and crystalline contributions) that low levels of crystallinity can make clear separation of the peaks difficult. None-the-less, even such apparently broad peaks can indicate the dominate crystal phase by main peak position and/or overall shape. There is a clear, continuous change in ^{15}N peak position from α-form for nylon 11 to γ-form for nylon 12.

Spin-Lattice Relaxation

The ^{13}C T_1 values for the copolymer series are contained in Table 4. The magnetization decay of the carbons (and the nitrogen) could be fit to multiple exponentials consistent with the behavior of semi-crystalline polymers with well-separated domains of differing mobilities (T_1 values differing by at least an order of magnitude). This is very different from glassy polymers that give multiple relaxation times of the same order of magnitude.[26] We believe the biexponetial behavior corresponds to amorphous phases with short relaxation times and ordered phases with longer times.

The T_1 behavior at first glance does not appear to follow a trend with respect to copolymer content. We propose that, at low comonomer contents, the small number of defects (mismatched repeat unit lengths) along the polymer backbones allow crystallization to occur more easily than in the homopolymer containing no defects as reflected by the increased T_1 values for the 15 mol-% copolymers (PA-2 and PA-6). As more defects are incorporated in the polymer backbone, however, the ability to form highly regular domains is diminished, decreasing the T_1 values below those of the

homopolymers. The all-trans carbons (C_{AT}) have the longest T_1 values of all the carbons except for the 50:50 copolymer. This suggests that the carbons are able to pack in ordered zig-zag arrays with little perturbation. The chemical shift for C_{AT} peak changes very little throughout the composition range indicating that gauche defects are not disrupting the planar zig-zag regions. Most likely the defects are associated with the methylenes attached directly to the amide units, allowing the middle of the hydrocarbon chains to assume the preferred all-trans conformation. The low T_1 values for C_α and C_β support this as do their chemical shifts which change with composition suggesting that conformational changes take place at these carbons.

Table 4.   Nylon 11-co-12 carbon-13 spin-lattice relaxation values (s)

SAMPLE	C_N	C_α	C_{AT}	C_β
PA-1	0.7 8.6	0.7 6.5	0.8 10.2	0.4 6.0
PA-2	0.8 6.5	0.6 9.3	0.9 12.3	0.4 7.4
PA-3	0.2 3.0	0.3 2.5	0.8 5.5	0.3 2.8
PA-4	0.6 5.8	0.5 2.2	0.6 3.2	0.3 3.0
PA-5	0.6 5.8	0.4 2.4	0.8 5.3	0.3 2.8
PA-6	0.7 9.1	0.7 12.9	1.3 14.1	0.4 5.1
PA-7	0.5 4.6	0.7 8.2	1.0 8.9	0.3 5.4

FTIR Analysis

Table 5[27] lists the FTIR bands between 1500 and 400 cm^{-1} while the spectra in this region are shown in Figure 5. Due to the thickness of the as-polymerized films, it was not possible to obtain accurate peak positions above 1500 cm^{-1}. Several prominent features can be seen that are common to all the spectra such as methylene scissoring (ca 1400) and twisting (ca 1300), the amide III (ca 1250), V (ca 690), and VI (ca 580) modes, and fundamental CH_2 rocking (ca 720).

PA-1 has three distinct bands in the scissoring region at 1468, 1456, and 1437 cm^{-1} which persist in the copolymers up to **PA-6** for which the lower frequency band becomes a shoulder. Copolymers more like α-nylon 11 have three bands in this region and the copolymers more like γ-nylon 12 have two bands, similar to behavior seen for nylon 12 samples with different amounts of α- and γ-phases.[27a] Three bands also appear in the twisting region near 1373, 1355, and 1339 cm^{-1}. However, the latter two bands are hardly discernable in **PA-5** and all of the bands shift to lower frequencies in **PA-6** and **PA-7**. The region of the amide III mode coupled to CH_2 wagging contains multiple bands that vary with composition. Samples **PA-1** through **PA-4** have bands near 1298 and 1278 cm^{-1} that shift to 1289 and 1271 cm^{-1} in the remaining copolymers. The amide III band (probably the band near 1270) is the most intense band in this region and is least sharp for the copolymer with the overall lowest carbon T_1 values, **PA-5**. The copolymers on either end of the composition range have low intensity but observable shoulders at slightly higher frequencies of the band near 1245 cm^{-1}, which is invariant over the composition range. The C-C skeletal bands (ca 1100 cm^{-1}) do not change from **PA-1** to **PA-7**.

Table 5. Nylon 11-co-12 FTIR bands (with relative intensities) observed for the region between 1500 and 400 cm^{-1}

PA-1	PA-2	PA-3	PA-4	PA-5	PA-6	PA-7	Assignment
1468 (3.31)	1467 (1.54)	1466 (2.11)	1467 (1.11)	1467 (3.48)	1466 (3.16)	1468 (2.02)	CH$_2$ scissoring
1457 (2.24)	1456 (1.20)	1457 (1.90)	1457 (0.76)	1456 (3.07)	1457 (2.69)	1457 (1.57)	
1437 (2.02)	1437 (1.12)	1436 (1.82)	1437 (0.70)	1436 (2.96)	1437 (2.61)	1437 (1.49)	
1419 (1.87)	1419 (1.04)	1420 (1.58)	1419 (0.53)	1421 (2.16)	1419 (1.86)		
1373 (1.78)	1373 (1.05)	1371 (1.65)	1371 (0.58)	1372 (2.38)			CH$_2$ twisting
					1369 (2.15)	1369 (1.26)	
1354 (1.65)	1356 (1.00)	1355 (1.54)	1353 (0.51)				
					1344 (1.83)	1342 (1.12)	
1340 (1.55)	1339 (0.96)	1338 (1.44)	1338 (0.46)	1338 (1.89)			
1310 (1.46)	1309 (0.93)	1310 (1.42)	1309 (0.44)	1308 (1.68)	1307 (1.72)	1306 (1.07)	
1296 (1.55)	1296 (0.97)	1296 (1.44)	1296 (0.46)				amide III coupled with CH$_2$ wagging
				1267 (2.05)	1269 (1.91)	1268 (1.17)	
1280 (1.85)	1278 (1.08)	1278 (1.64)	1277 (0.56)				
				1273 (2.24)	1271 (2.07)	1270 (1.25)	
1262 (1.62)	1262 (0.99)	1262 (1.52)					
1244 (1.70)	1244 (1.01)	1247 (1.53)	1246 (0.50)	1245 (2.01)	1245 (1.87)	1244 (1.16)	
1224 (1.74)	1225 (1.02)	1225 (1.46)	1225 (0.46)	1225 (1.82)	1223 (1.68)	1222 (1.07)	

1199 (1.26)	1199 (0.85)	1198 (1.21)	1200 (0.33)				
1192 (1.13)	1193 (0.84)	1193 (1.23)	1194 (0.34)	1194 (1.46)	1193 (1.40)	1193 (0.81)	splitting of amide III and C-C skeletal motions
1161 (1.18)	1161 (0.83)	1160 (1.20)	1160 (0.35)	1161 (1.58)	1161 (1.63)	1161 (1.05)	
1125 (1.13)	1124 (0.81)	1123 (1.10)	1123 (0.29)	1122 (1.31)	1123 (1.27)	1122 (0.90)	
	1107 (0.73)	1108 (0.84)	1109 (0.21)	1109 (1.03)	1110 (1.03)	1110 (0.81)	
1083 (0.86)	1081 (0.71)	1081 (0.85)	1081 (0.18)	1064 (0.93)			CONH skeletal vibrations
1059 (0.90)	1059 (0.73)	1061 (0.86)	1063 (0.20)	1065 (1.03)	1065 (1.06)	1064 (0.82)	
1025 (0.66)	1025 (0.71)	1027 (0.82)	1028 (0.17)	1028 (0.92)	1028 (0.95)	1028 (0.79)	
					1011 (0.69)	1011 (0.76)	
997 (0.88)	997 (0.72)	997 (0.72)	994 (0.17)				
				960 (0.90)	962 (0.90)	962 (0.76)	
974 (0.86)		972 (0.82)	973 (0.17)				
967 (0.86)	967 (0.71)						
937 (0.96)	938 (0.74)	940 (0.85)	942 (0.19)	944 (0.99)	946 (1.02)	946 (0.81)	
					905 (0.82)	905 (0.70)	
722 (1.90)	722 (1.10)	721 (1.62)	722 (0.60)	722 (2.55)	723 (2.26)	723 (1.31)	fundamental CH_2 rocking
687 (1.44)	689 (0.93)	691 (1.24)	692 (0.37)	sh			amide V
626 (1.02)	625 (0.78)	626 (0.96)	624 (0.25)	627 (1.21)	626 (1.19)	626 (0.86)	
563 (1.16)	565 (0.82)	588 (1.01)	592 (0.26)	583 (1.19)	593 (1.09)	592 (0.84)	amide VI
545 (0.95)	542 (0.75)	540 (0.83)	540 (0.20)	538 (1.02)	538 (1.03)	538 (0.80)	

The CONH skeletal motion bands between 1084 and 905 cm^{-1} are well-defined in all of the copolymers except PA-5. The pattern of bands changes at this composition point also. The fundamental rocking mode for methylenes appears constant over the copolymer series. The bands for amide V and VI show changes which correspond to the changes seen in the NMR spectra. The amide V peak, which consists of two bands near 690 and 628 cm^{-1}, shifts from 687 to a weak shoulder in PA-1 to PA-5, respectively, and is absent in the remaining two spectra of copolymers high in nylon 12 content. The lower frequency band remains near 628 but decreases in relative intensity with increasing nylon 12 content. Two bands associated with the amide VI mode shift over the copolymer composition range. For PA-1, a peak appears at 583 shifting to 592 for PA-7 and decreasing in relative intensity, which suggests that there is a shift from the α-phase to the γ-phase. The second band at 545 cm^{-1} for PA-1 moves to lower frequencies on increasing the nylon 12 content, ending at 538 cm^{-1} for PA-7.

X-Ray Analysis

The wide-angle X-ray diffraction patterns for the copolymer series confirm the complimentary nature of structural analysis with techniques that observe different levels of organization. The NMR and FTIR data provide molecular level information which, for crystalline domains, indicates the conformation and packing of repeat unit segments. X-ray, on the other hand, sees arrays of molecular segments that correspond to higher levels of organization built up from the molecular to the microscopic level. It is often the case that contributions from one of the domains present may make observation of the others difficult. For example, the broad amorphous peak in the ^{15}N NMR spectra of PA-1

(Figure 4) masks the α-crystal peak which is clearly seen as a pair of peaks at 2θ values of 20.2 and 22.8 in the X-ray diffraction pattern (Figure 6). These are typical values for α-crystallites.[28]

The strong NMR peaks for the γ-form of nylon 12 (PA-7, Figures 2 and 4) are consistent with the strong, relatively narrow X-ray peak seen for this sample at a value (2θ = 21.3) characteristic for γ-crystallites. The X-ray patterns for the mostly-γ copolymers (by NMR and IR), PA-6 and PA-5, are virtually identical to that of PA-7. However, the pattern for PA-4 is almost the same in peak width and position (2θ = 21.4), yet NMR and IR indicate weak α or some intermediate form with a mixture of weak α and γ peaks. Even more surprising are the broad X-ray peak for PA-3 and the intermediate pair of peaks (2θ = 20.6 and 22.1) for PA-2. The NMR and IR data are consistent with strong α-content for both. We believe this is indicative of less-ordered crystallites for the copolymers as the compositions move away from the two extremes, a change which is more easily seen for the α-form samples (because it normally gives two, widely separated peaks in the X-ray pattern) than for the γ samples which display a single X-ray peak which overlays the broad peak of the pseudo-hexagonal or mesomorphic peak that occurs in many quenched or disordered nylon samples.[29] The combination of spectral and X-ray data gives a good qualitative picture of the molecular and microscopic order in these as-polymerized copolymer samples. The additional question of what effect sample treatment has on the type and degree of ordered phase present is also well determined by this combination of methods as illustrated for the ^{15}N-labelled 1:1 copolymer (PA-4) below.

[15]N-Enriched 1:1 Copolymer: Sample Treatment Effects

The polymorphism of homopolyamides has been repeatedly demonstrated but the question remains of polymorphic crystallinity in random copolyamides. Sample history and treatment affect the type and amount of crystallinity, even to the point of almost completely generating the thermodynamically less-stable of the crystal forms available to a given polyamide.[14,15] We subjected an isotopically enriched 50 mol-% nylon 11 sample, PA-4, to different chemical and thermal treatments to evaluate their affect on crystallinity. The copolymer sample was prepared from a 1:1 mixture of 50 mol-% isotopically-enriched amino acids to give a 50 mol-% nylon 11 copolymer (PA-4) with 50 % total ^{15}N enrichment. The ^{15}N-labelled samples were given no treatment (as-polymerized, PA-4); dissolved in 2,2,2-trifluoroethanol and methylene chloride (3:2 by volume) and cast on a glass plate (PA-4CF); precipitated from the mixture into diethyl ether, collected and dried (PA-4PF); and the latter two annealed separately under vacuum in sealed glass tubes at 115 °C for 12 h (PA-4CA and PA-4PA, respectively).

The ^{13}C and ^{15}N solid-state NMR spectra are shown in Figures 7 and 8, respectively, while the X-ray diffraction patterns of the five samples are given in Figure 9. The chemical shift values for both ^{13}C and ^{15}N spectra are included in Table 3, while the thermal data are contained in Table 2. In Figure 7, the samples cast onto glass and simply dried (PA-4CF) or annealed at 115 °C (PA-4CA) show peaks characteristic of the γ-crystal form. In fact, the ^{15}N NMR peaks at 89 ppm (Figure 8) confirm this as do the sharp X-ray peaks at $2\theta = 21.3$. Solvent casting onto glass plates is clearly an effective method for inducing highly ordered γ-crystals into copolymers of nylons 11 and 12.

Also interesting is the behavior displayed by the other three samples (**PA-4, PA-4PF and PA-4PA**) whose spectra and diffraction patterns are given in the upper, middle and bottom traces of Figures 7, 8 and 9. The ^{13}C peaks appear to indicate α-form crystallites in all three samples and the chemical shifts listed in Table 3 support this. In fact, neither the ^{15}N CPT1 traces nor the X-ray diffraction patterns confirm this. Instead, both suggest disordered structures based on broad peaks centered at the amorphous positions, with the ^{15}N NMR peaks showing virtually no shoulder at 84 ppm as seen for the **PA-1** through **PA-3** spectra in Figure 4. However, it should be remembered that the CPT1 method (right-hand set of peaks in Figures 7 and 8) selectively observes crystalline, or at least more rigid, domains. The samples may contain chains packed in a pseudohexagonal crystalline array which gives a ^{15}N peak position similar to that of the amorphous phase as well as the mesomorphic form and the high-temperature δ-crystals of nylon 11.[14]

Let us now consider the effects of different treatments on the spin-lattice relaxation values of PA-4 samples (see Table 6). The precipitated sample has the overall lowest values with annealing having very little affect on the carbon T_1 values. However, the T_{1N} value nearly doubles and a component with a very short T_1 appears on annealing. The increase in the nitrogen T_1 values with little change in the carbon values on annealing suggests that for this sample, ordering occurs near the amide units with little change in the hydrocarbon segments. The ^{15}N CPT1 peak shape also narrows for this sample on annealing (from 5.6 ppm wide at half height to 4.8 ppm), and the main peak shifts upfield from 87.2 to 86.4 ppm.

The cast sample (PA-4CF) has the longest carbon T_1 values of those presented here, indicating that solvent casting forms a highly ordered phase that is thermally stable. Annealing increases this order, as reflected by the T_1 values for the carbons immediately adjacent to the amide group and for the amide nitrogen itself. Again, the amide order dominates and the hydrocarbon segments are less ordered.

Table 6.   PA-4 carbon-13 and nitrogen-15 spin-lattice relaxation values (s)

SAMPLE	C_N	C_α	C_{AT}	C_β	NH[a]
PA-4CF	1.7 6.3	0.3 2.5	0.4 20.3	0.4 4.1	0.1 6.8 112.9
PA-4PF	0.5 2.5	0.3 1.5	0.7 3.8	0.3 1.6	3.0 22.6
PA-4CA	0.8 12.5	0.9 15.9	1.2 13.3	0.3 4.2	1.6 39.4 349.4
PA-4PA	0.3 1.4	0.3 2.4	0.8 4.3	0.3 1.7	0.3 5.9 42.8

[a] - compare to T_{1N} values for nylon 11:[14] quenched sample; 2.3 s / 13.4 s, and annealed sample; 4.9 s / 68.1 s, and for nylon 12:[15] quenched sample; 3.0 s / 34.0 s, and annealed sample; 20.0 s / 314.0 s.

The high degree of order for the cast film sample (especially after annealing), indicated by the sharpness of the γ-form ^{15}N NMR peak at 89.1 and the very long T_{1N} values, is consistent with the DSC ΔH value measured: it was the highest of any of the samples examined here despite the fact that the T_m did not change. Two observations are important to make here. First, despite the fact that the 1:1 copolymer should be

highly disordered due to random monomer sequences, sample treatment can induce a very high degree of order. Second, once an ordered phase is formed (at least for nylons 11, 12 and their copolymers), annealing does not cause transformation to other, supposedly more stable, phases. In fact, annealing actually increases the order in the existing ordered domains as indicated by narrowing of the ^{15}N NMR peak and the X-ray diffraction pattern, and a doubling of the T_{1N} value.

Conclusions

The nylon 11-co-12 series prepared here shows the expected melting point depression (for as-polymerized samples) with the lowest T_m and percent crystallinity belonging to PA-5, the 65 mol-% nylon 12 copolymer. This is also the copolymer with the overall lowest carbon T_1 values. From solid-state NMR ^{13}C and ^{15}N line shapes and positions, the crystalline phase that dominates up to 65 mol-% nylon 12 is the α-phase. The γ-phase is present in copolymers with higher nylon 12 mol-%. Several bands in the FTIR spectra reflect a similar trend. The pattern of bands in the amide III region changes noticeably at PA-5 as do the CONH skeletal motion bands.

The ^{15}N-labelled 1:1 copolymer (PA-4) was shown to be polymorphic in nature. As-polymerized and precipitated flakes possessed an ordered phase with α-like characteristics in the NMR and IR spectra but which appears to be pseudohexagonal by X-ray. A strong γ-like phase was observed in the solvent cast sample. Neither phase for PA-4 could be transformed into the other by annealing, which actually increased the degree of existing order.

Overall, it is clear that sample history and composition are both important in determining the degree and type of crystallinity and/or order in nylon copolymers. Vital to observation and understanding of molecular and microscopic behavior is the use of a combination of analytical methods which "see" different functional groups (amides versus methylene chains), backbone segments and conformations, and arrays of segments and polymer chains in crystallographic domains.
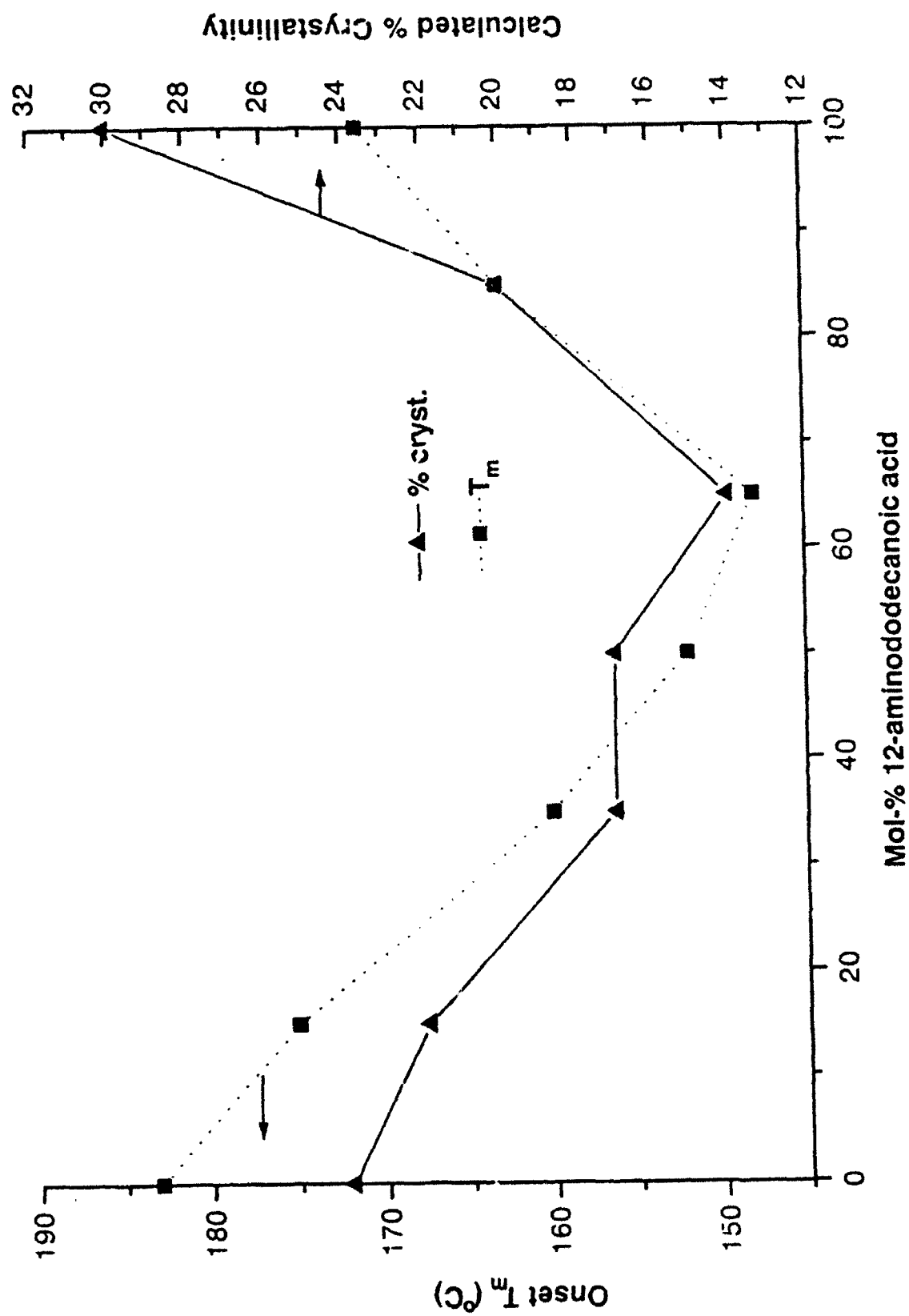
References

1. Muthiah, J.; Mathias, L. J. *J. Polym. Sci., Polym. Chem. Ed.* 1991, *29*, 29.

2. Nair, C. P. R. *Macromolecules* 1993, *26*, 47.

3. Arai, M.; Cassidy, P. E.; Farley, J. M. *Macromolecules* 1989, *22*, 989.

4. Evers, R. C.; Dnag, T. D.; Moore, R. D. *J. Polym. Sci., Polym. Chem. Ed.* 1993, *29*, 121.

5. Gaudiana, R. A.; Sinta, R. F. *J. Polym. Sci., Polym. Chem. Ed.* 1991, *29*, 45.

6. McCormick, C. L.; Elliot, D. L. *Macromolecules* 1986, *19*, 542.

7. Feng, X. D.; Voong, S. T.; Song, C. X.; Chen, W. Y. *J. Polym. Sci., Polym. Lett. Ed.* 1983, *21*, 593.

8. Kricheldorf, H. R.; Mang, T.; Jonté, J. M. *Macromolecules* 1984, *17*, 2173.

9. Mitomo, H.; Barham, P. J.; Keller, A. *Polym. J.* 1987, *19*, 1241.

10. Kamiya, N.; Sakurai, M.; Inoue, Y.; Chûjô, R. *Macromolecules* 24, 3888 (1991).

11. Yu, L.; Chen, M.; Dalton, L. R. *J. Polym. Sci., Polym. Chem. Ed.* 1991, *29*, 127.

12. Buchanan, C. M.; Gedon, S. C.; White, A. W.; Wood, M. D. *Macromolecules* 1992, *25*, 7373.

13. Powell, D. G.; Mathias, L. J. *J. Am. Chem. Soc.* 1990, *112*, 669.

14. Mathias, L. J.; Powell, D. G.; Autran, J.-P.; Porter, R. S. *Macromolecules* 1990, *23*, 963.

15. Mathias, L. J.; Johnson, C. G. *Macromolecules* 1991, *24*, 6114.

16. D. A. Torchia, *J. Magn. Reson.*, *30*, 613 (1978).

17. Kricheldorf, H. S.; Hull, W. E. *J. Polym. Sci., Polym. Chem. Ed.* 1978, *16*, 2253.

18. (a) Kobayyashi, F.; Matsuya, K. *J. Polym. Sci., Part A* 1963, *1*, 111. (b) Hybart, F. J.; Pepper, B. *J. Appl. Polym. Sci.* 1969, *13*, 2643. (c) Kubota, H.; Nowell, J. B. *J. Appl. Polym. Sci.* 1975, *19*, 1521. (d) Goodman, I.; Kehayoglou, A. H. *E. Polym. J.* 1983, *19*, 321. (e) Kehayoglou, A. H.; Arvanitoyannis, I. *Eur. Polym. J.* 1990, *26*, 261. (f) Gonsalves, K. E.; Chen, X. *Polym. Commun.* 1990, *31*, 312. (g) Coutin, B.; Sekiguchi, H.; Prieto, A.; Munoz-Guerra, S. *Makromol. Chem.* 1991, *192*, 21.

19. (a) Kricheldorf, H. R.; Leppert, E.; Schilling, G. *Makromol. Chem.* 1975, *176*, 81. (b) Kricheldorf, H. R.; Schilling, G. *Makromol. Chem.* 1976, *177*, 607. (c) Kricheldorf, H. R.; Hull, W. E. *J. Macromol. Sci.-Chem.* 1977, *A11*, 2281. (d) Kricheldorf, H. R.; Coutin, B.; Sekiguchi, H. *J. Polym. Sci., Polym. Chem. Ed.* 1982, *20*, 2353. (e) Kricheldorf, H. R.; Joshi, S. V.; Hull, W. E. *J. Polym. Sci., Polym. Chem. Ed.* 1982, *20*, 2791.

20. Garner, D. P.; Fasulo, P. D. *J. Appl. Polym. Sci.* 1988, *35*, 495.

21. Xenopoulos, A.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* 1990, *28*, 2271.

22. Johnson, C. G.; Mathias, L. J., manuscript submitted for publication in *Polymer Comm.*

23. Puffr, R.; Kubának, V. *Lactam-Based Polyamides*; CRC Press: Boca Raton, FA, Vol. 1, 1992.

24. Johnson, C. G.; Mathias, L. J. *Polymer*, in press.

25. Hatfield, G. R.; Glans, J. H.; Hammond, W. B. *Macromolecules* 1990, *23*, 1654.

26. Schaffer, J.; Sefcik, M. D.; Stejskal, E. O.; McKay, R. A.; Dixon, W. T.; Cais, R. E. *Macromolecules* 1984, *17*, 1107.

27. (a) Ishikawa, T.; Nagai, S.; Kasai, N. *J. Polym. Sci., Polym. Phys. Ed.* 1980, *18*, 291. (b) Matsubara, I.; Otoh, Y.; Shinomiya, M. *Polym. Letts.* 1966, *4*, 47.

28. Hiramatsu, N.; Haraguchi, K.; Hirakawa, S. *Jpn. J. Appl. Phys.* 1983, *22*, 335.

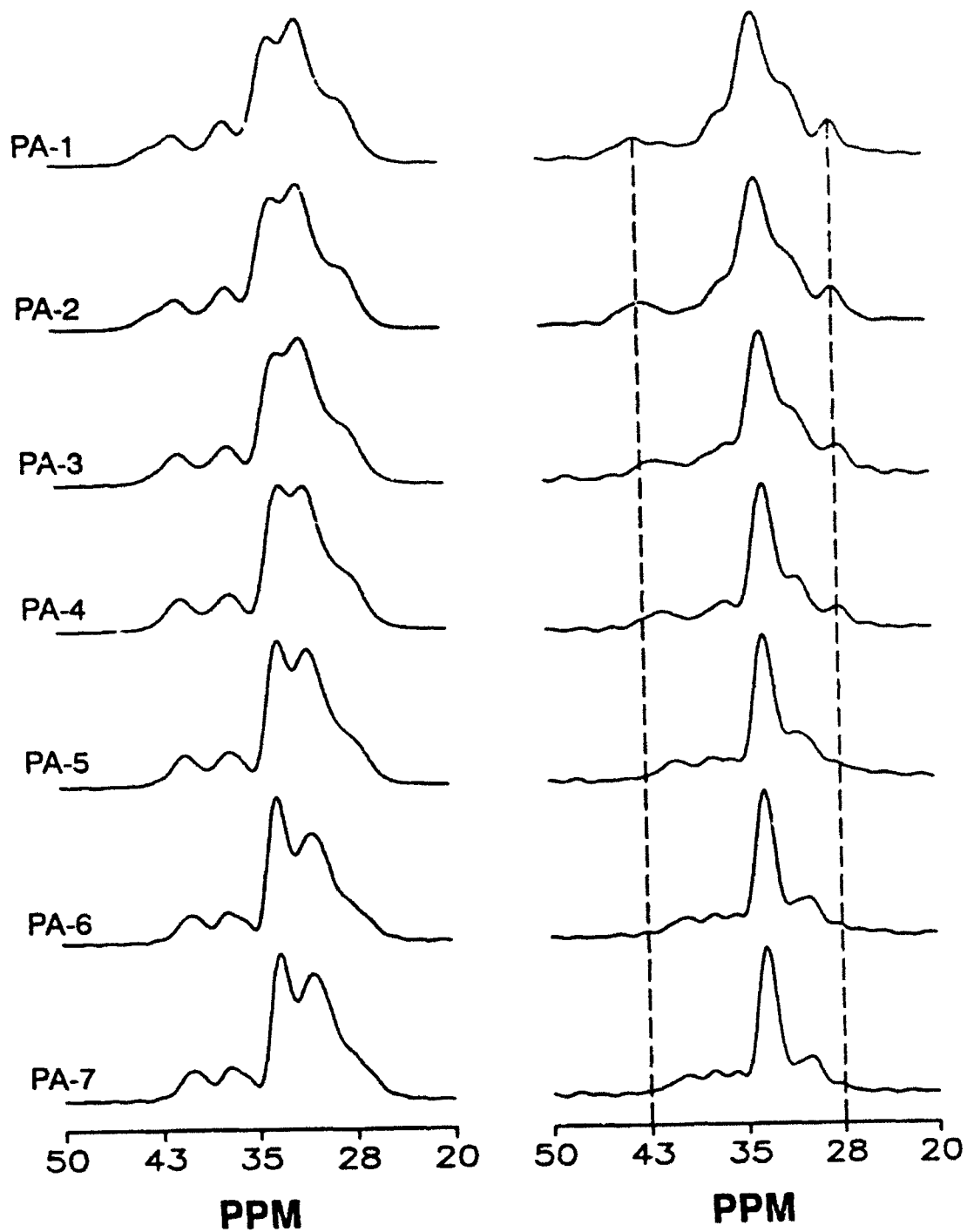29.   Kim, K. G.; Newman, B. A.; Scheinbeim, J. I. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 2477.
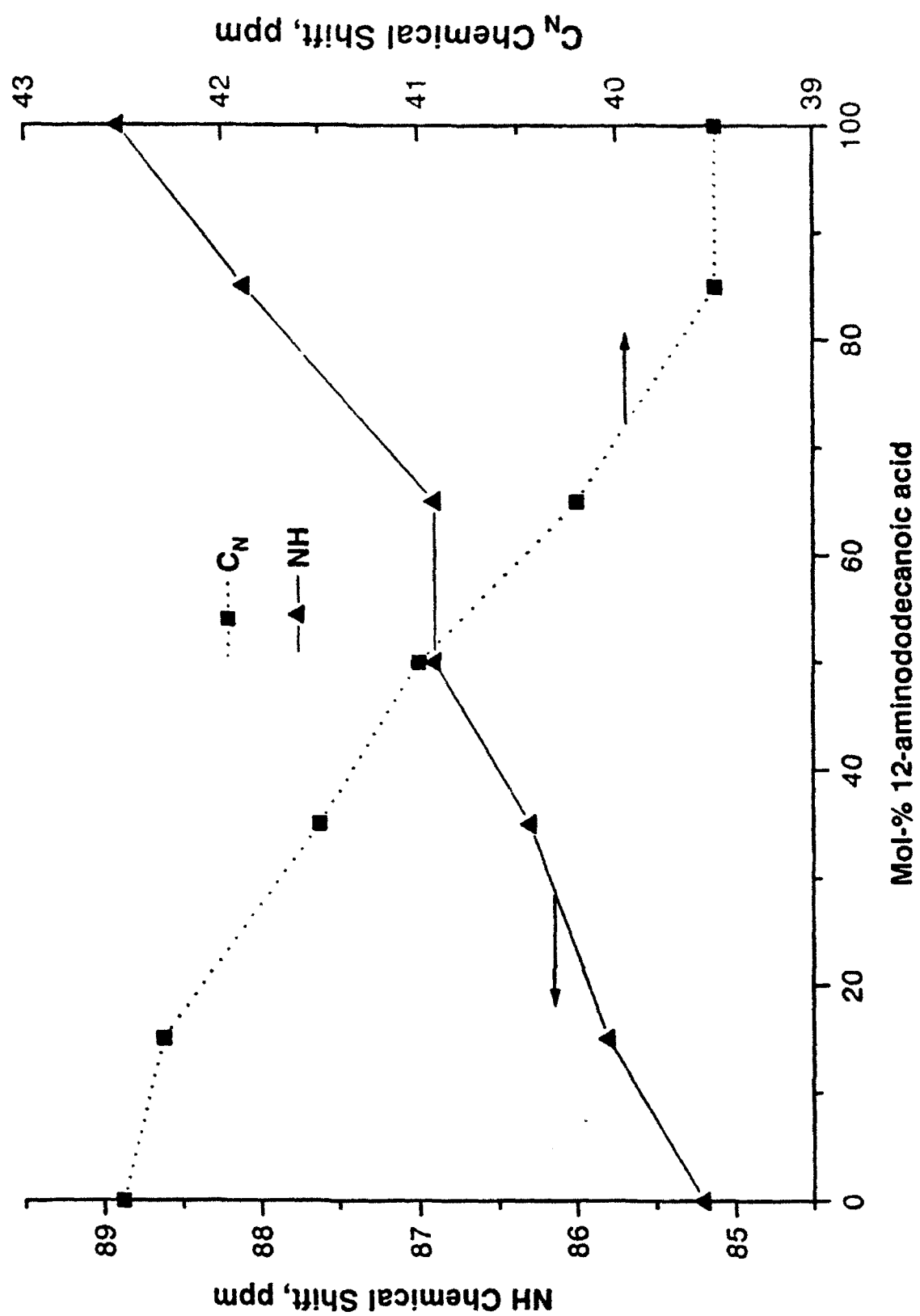
List of Figures

Calculated % Crystallinity

Onset T_m (°C)

Mol-% 12-aminododecanoic acid

—▲— % cryst.

■ T_m

PA-1
PA-2
PA-3
PA-4
PA-5
PA-6
PA-7

50   43   35   28   20
PPM

50   43   35   28   20
PPM

Johnson, Fig 2

PA-1

PA-2

PA-3

PA-4

PA-5

PA-6

PA-7

110   100   90   80   70

PPM

PA-1

PA-2

PA-3

PA-4

PA-5

PA-6

PA-7

10 12 14 16 18 20 22 24 26 28 30

2-theta

PA-4

PA-4CF

PA-4PF

PA-4CA

PA-4PA

50   43   35   28   20
PPM

50   43   35   28   20
PPM

PA-4

PA-4CF

PA-4PF

PA-4CA

PA-4PA

110 100 90 80 70
PPM

110 100 90 80 70
PPM

PA-4

PA-4CF

PA-4PF

PA-4CA

PA-4PA

10 12 14 16 18 20 22 24 26 28 30

2-theta

Fig. 9